START

# Internal Letter

Rockwell International

Date: June 29, 1984

No. 65453-84-163

TO: (Name, Organization, Internal Address)

L. M. Sasaki
Waste Management Systems Engineering
2750E/A227/200 East Area

FROM: (Name, Organization, Internal Address, Phone)

M. T. Jansky / B. A. Meissner
Chemical Laboratory
MO-037/222S/200 West Area
3-1571



Subject: Thermal Destruction of Complexants

Ref: Letter, 65453-84-079, March 23, 1984, M. T. Jansky/B. A. Meissner to L. M. Sasaki, "Proposed Laboratory Experiments to Study High-Temperature Decomposition of Complexants"

Organics present in Hanford waste have reduced optimum waste volume reduction (WVR) during waste processing by either (a) inhibiting maximum WVR in the evaporator-crystallizer or (b) enhancing slurry growth in the storage tank after concentration. The removal of the organics (specifically HEDTA and EDTA), or at least lowering their concentration, may enhance the minimization of storage volume, with subsequent savings of dollars. The referenced letter outlined preliminary experiments which would be used to examine thermal destruction of the organics. Much of the preliminary work has been completed and is discussed below.

A feed solution similar to that used in the September 1983 pilot plant double-shell slurry (DSS) run was prepared. The analysis of the feed showed that desired concentrations were almost achieved (see Table I). A portion of the standard feed solution was spiked with organics and used to test for thermal destruction of complexants. The spiked feed was also analyzed, and those results are also shown in Table I.

Each feed was subjected to the following experimentation: One aliquot was concentrated, using the lab-scale batch boildown apparatus, to a "maximum" WVR at constant pressure. A second aliquot was heated, for 48 hours, at 140°C prior to concentration. A third aliquot was heated, also for 48 hours, at 240°C prior to concentration. Both heated aliquots were also analyzed prior to boildown. The "treated" feeds' (i.e., preheated) analyses are shown in Table II.

The preheating treatment flared several problems when attempting the elevated temperatures. The stainless steel Parr bombs utilized rubber o-rings for maintaining an airtight environment. The o-rings failed at the elevated temperatures, causing the contents of the bombs to solidify due to evaporation. The synthetics, sans organics, turned into a hard cake; whereas when organics were present, the contents turned into "cookie dough". The bombs were revamped using Teflon-wrapped o-rings, and the synthetics were successfully heated.

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After storing the DSS for four weeks at 80°C, the major change was a reduction in aluminum concentrations. As shown in Table VI, the soluble aluminum content in the slurry was less in every case. There were insoluble solids present after the four-week storage period; therefore, those mixtures were filtered and analyzed. This phenomenon is supported by the knowledge of slow aluminum kinetics.

Overall, the growth and gas generation seem to be consistent. When considering growth and gas generation, viscosity data correlate well. The more viscous materials (see Tables V and VII) had more growth and less gas generation (i.e., more entrapment). Conversely, the less viscous materials did not grow as much; but more gas generation was observed.

The one, unusual observation is that even though great quantities of gas were generated, no glaring changes in chemical compositions were observed. At this time, there is no reason to suspect that the integrity of the laboratory apparatus failed. All indications are that the vessels maintain a closed environment, which leaves the question as to the source of gas unanswered.

This letter satisfies a June 29, 1984 milestone. Additional work is recommended to follow up this study. Specifically, experiments examining (a) minimal temperature required for thermal destruction, (b) effects of time of heating versus temperature, and (c) chemical composition effects. To that end, the Chemical Laboratory Unit recommends that a statistically designed parameter study be drafted with multiple temperatures, times, and concentrations integrated into the study. Please call if you desire the Chemical Laboratory Unit to pursue the thermal destruction experiments.

David Herting for MTJ
M. T. Jansky
Chemist

B. A. Meissner
B. A. Meissner
Parachemist

MTJ/BAM/pdk

Att.

cc: D. R. Bratzel
J. S. Buckingham DLN for JSB
K. G. Carothers
C. H. Delegard
D. L. Herting
T. B. Veneziano
File Code WB

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TABLE I

Composition of Synthetic Thermal Destruction Feeds

| Component | Concentration (Moles/Liter) | | |
|---|---|---|---|
| | Without Organics | | With Organics |
| | Theoretical | Analyzed | |
| $Al^{+3}$ | 1.23 | 1.24 | 1.18 |
| $OH^-$ | 3.40 | 3.34 | 3.27 |
| $CO_3^{-2}$ | 0.16 | 0.182 | 0.175 |
| TOC(g/L) | -- | 3.03 | 17.80 |
| $NO_2^-$ | 2.15 | 2.03 | 2.15 |
| $NO_3^-$ | 2.50 | 2.74 | 2.61 |
| EDTA | -- | -- | 0.0413 |
| HEDTA | -- | -- | 0.0773 |
| Sp. G.* | | 1.41 | 1.42 |

*Room Temperature

TABLE II

Composition of Pre-Heated Feeds
(Held at Temperature for 48 hours)

| Component | Concentration (Moles/Liter) | | | |
|---|---|---|---|---|
| | Sans Organics | | Organics | |
| | 140°C | 240°C | 140°C | 240°C |
| $Al^{+3}$ | 1.31 | 1.27 | 1.30 | 1.29 |
| $OH^-$ | 3.59 | 3.35 | 3.31 | 2.93 |
| $CO_3^{-2}$ | 0.186 | 0.191 | 0.219 | 0.890 |
| TOC(g/L) | 3.17 | 0.27 | 19.4 | 4.13 |
| $NO_2^-$ | 2.11 | 2.15 | 1.75 | 0.88 |
| $NO_3^-$ | 2.72 | 3.97* | 2.71 | 2.37 |
| EDTA | -- | -- | 0.590** | ND |
| HEDTA | -- | -- | 0.637** | ND |
| Sp. G.*** | 1.44 | 1.49 | 1.44 | 1.44 |
| % $H_2O$ | 53.7 | 55.3 | 44.9 | 53.6 |

*Initial concentration 2.8 M, but solids were present. The mixture was filtered, with the resulting 3.97 M. The crystals appeared to be phosphate needles.

**Believed to be off by a factor of 10. Questionable data.

***Room Temperature.

TABLE III

Boildown Data for Feeds

| Observation | Feed Type | | | | | |
|---|---|---|---|---|---|---|
| | Sans Organics | | | Organics | | |
| | Control | 140°C | 240°C | Control | 140°C | 240°C |
| Initial Temperature[a] (°C) | 53.6 | 54.2 | 53.2 | 53.6 | 53.6 | 51.8 |
| Nucleation Point (% WVR) | 25 | 18 | 23 | 32 | 29 | * |
| Nucleation Temperature[b] (°C) | 62.0 | 60.4 | 59.8 | 65.0 | 62.5 | * |
| Final Temperature[c] (°C) | 73.4 | 74.8 | 71.4 | 74.0 | 72.6 | 72.0 |

[a] Boiling point, at 60 torr, at 0 % WVR.

[b] Boiling point, at 60 torr, when nucleation occurred.

[c] Boiling point, at 60 torr, at 45% WVR.

* The 240°C/organics feed had solids present when the boildown was begun.

TABLE IV

Chemical Compositions of Concentrated Products
(45% WVR, 60 torr)

| Component | Concentration (Moles/Liter) | | | | | |
|---|---|---|---|---|---|---|
| | Sans Organics | | | Organics | | |
| | Control | 140°C | 240°C | Control | 140°C | 240°C |
| $Al^{+3}$ | 2.23 | 2.20 | 2.18 | 2.08 | 2.05 | 2.28 |
| $OH^-$ | 6.05 | 5.95 | 5.90 | 5.70 | 5.73 | 5.15 |
| $CO_3^{-2}$ | 0.37 | 0.34 | 0.32 | 0.34 | 0.40 | 1.53 |
| TOC(g/L) | 1.3 | 0.97 | 0.86 | 32.25 | 37.75 | 9.25 |
| $NO_2^-$ | 3.75 | 3.68 | 3.60 | 3.83 | 3.55 | 2.52 |
| $NO_3^-$ | 4.33 | 4.64 | 4.40 | 4.1 | 4.00 | 4.17 |
| EDTA | -- | -- | -- | 0.085 | 0.076 | ** |
| HEDTA | -- | -- | -- | 0.159 | 0.113 | ** |
| Sp. G.* | 1.65 | 1.69 | 1.63 | 1.62 | 1.65 | 1.68 |
| % $H_2O$ | 32.30 | 28.70 | 30.49 | 30.61 | 30.60 | 35.67 |

* 80°C
** Non-detectable

TABLE V

Viscosity Data for Concentrated Products
(45% WVR, 60 torr)

| Shear** | Viscosity (cp)* | | | | | |
|---|---|---|---|---|---|---|
| | Sans Organics | | | Organics | | |
| | Control | 140°C | 240°C | Control | 140°C | 240°C |
| 256 | 17 | 15 | 17 | 22 | 47 | 26 |
| 128 | 19 | 14 | 17 | 26 | 49 | 27 |
| 64 | 26 | 15 | 21 | 38 | 51 | 33 |
| 128 | 19 | 14 | 18 | 24 | 49 | 27 |
| 256 | 17 | 16 | 16 | 21 | 46 | 25 |

* Viscosity determined at 80°C using Haake Rotovisco Absolute viscometer.

** Viscosity measured by initially decreasing the shear rate, subsequently increasing the shear.

TABLE VI

Chemical Compositions of Concentrated Products After 4.5 Weeks
(45% WVR, 60 torr, stored at 80°C)

Concentration (Moles/Liter)

| Component | Sans Organics | | | Organics | | |
|---|---|---|---|---|---|---|
| | Control | 140°C | 240°C | Control | 140°C | 240°C |
| $Al^{+3}$ | 1.66 | 1.62 | 1.64 | 1.60 | 1.44 | 1.75 |
| $OH^-$ | 6.05 | 6.05 | 6.15 | 5.75 | 5.75 | 5.10 |
| $CO_3^{-2}$ | 0.34 | 0.36 | 0.35 | 0.34 | 0.46 | 1.48 |
| TOC (g/L) | 0.94 | 0.77 | 17.8*** | 36.45 | 31.55 | 9.0 |
| $NO_2^-$ | 3.75 | 3.68 | 3.80 | 3.63 | 3.49 | 2.33 |
| $NO_3^-$ | 4.36 | 4.36 | 4.47 | 4.23 | 4.32 | 4.21 |
| EDTA | -- | -- | -- | 0.12 | 0.11 | ** |
| HEDTA | -- | -- | -- | 0.16 | 0.083 | ** |
| SpG* | | | | | | |
| % $H_2O$ | 30.30 | 37.70 | | 32.51 | 27.80 | 32.10 |

* 80°C.
** Below Detection Limits.
*** Questionable result.

## TABLE VII

### Viscosity Data for Stored DSS
(80°C, 4.5 Weeks)

Viscosity (cp)**

| Shear* | Sans Organics | | | Organics | | |
|---|---|---|---|---|---|---|
| | Control | 140°C | 240°C | Control | 140°C | 240°C |
| 256 | 16 | 15 | 15 | 49 | 88 | 20 |
| 128 | 17 | 13 | 13 | 58 | 71 | 24 |
| 64 | 19 | 14 | 15 | 77 | 77 | 28 |
| 128 | 17 | 13 | 14 | 63 | 68 | 24 |
| 256 | 16 | 15 | 17 | 52 | 60 | 23 |

* Viscosity measured by initially decreasing the shear rate and subsequently increasing the shear.

** Viscosity determined at 80°C using Haake Rotovisco Absolute viscometer.

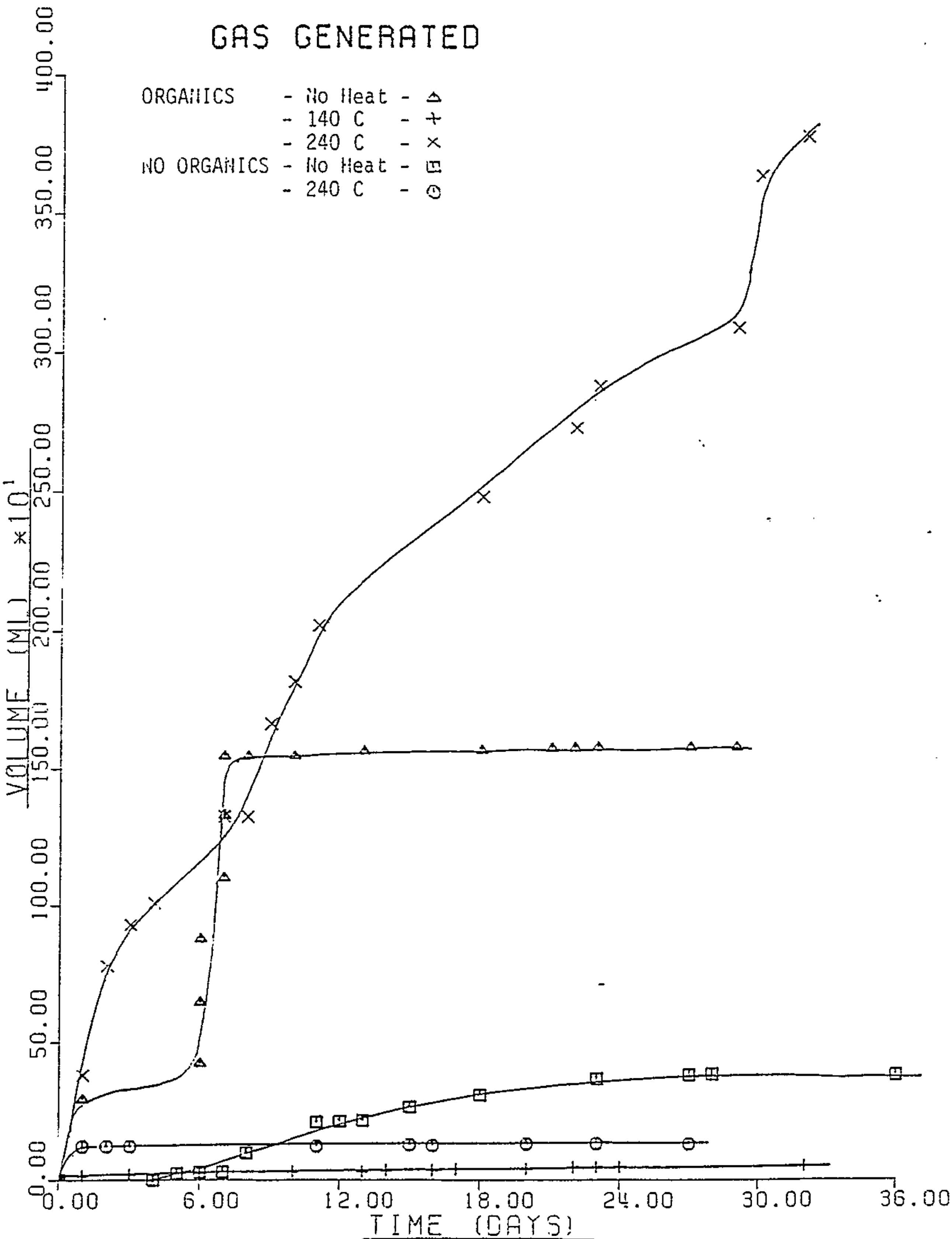


FIGURE 1. GAS GENERATION OF DSS AT 80°C.

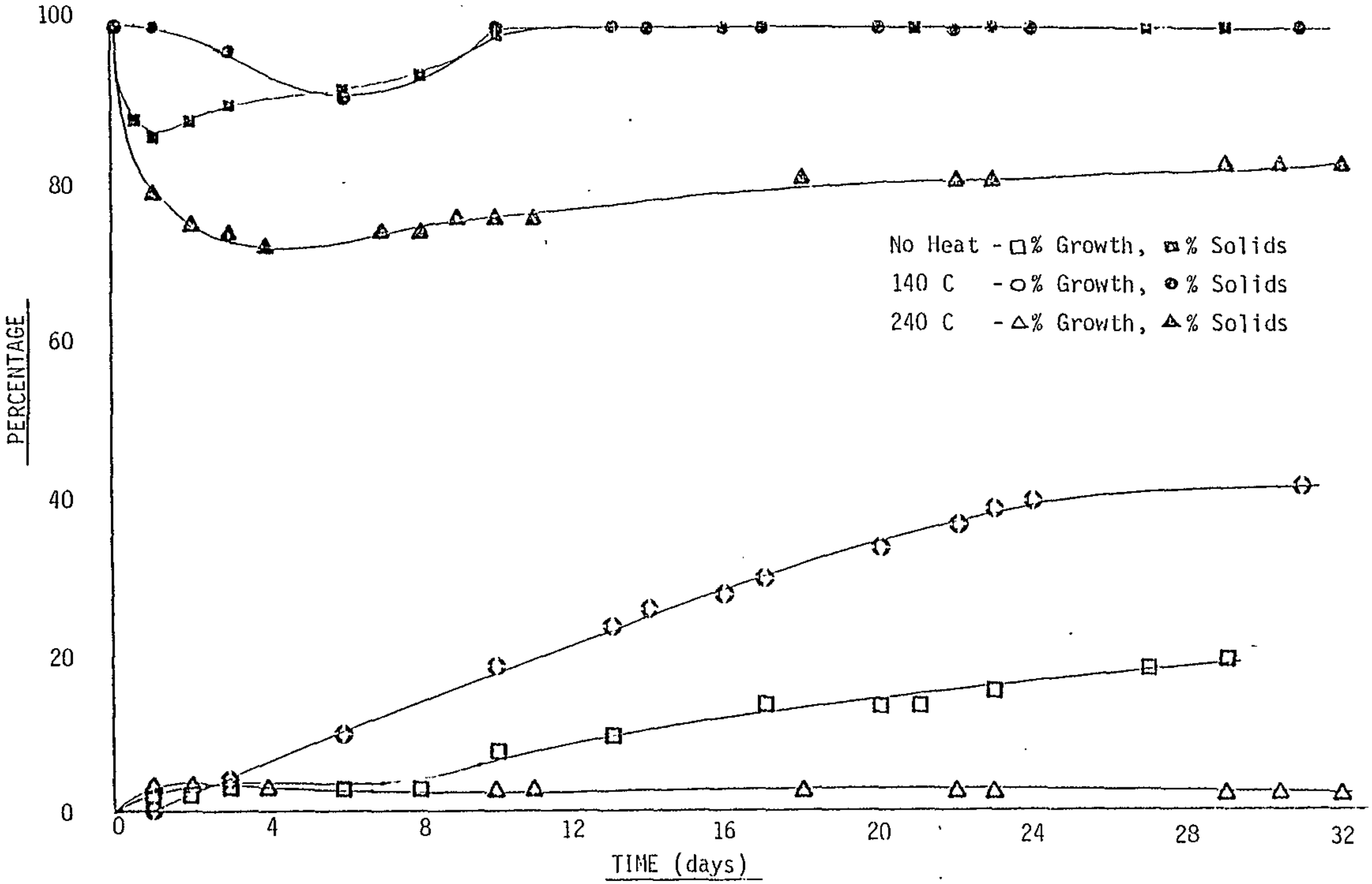


FIGURE 2. A Comparison of Volume Percent Solids and Volume Percent Growth versus Time of DSS Containing Organic Complexants (HEDTA/EDTA).

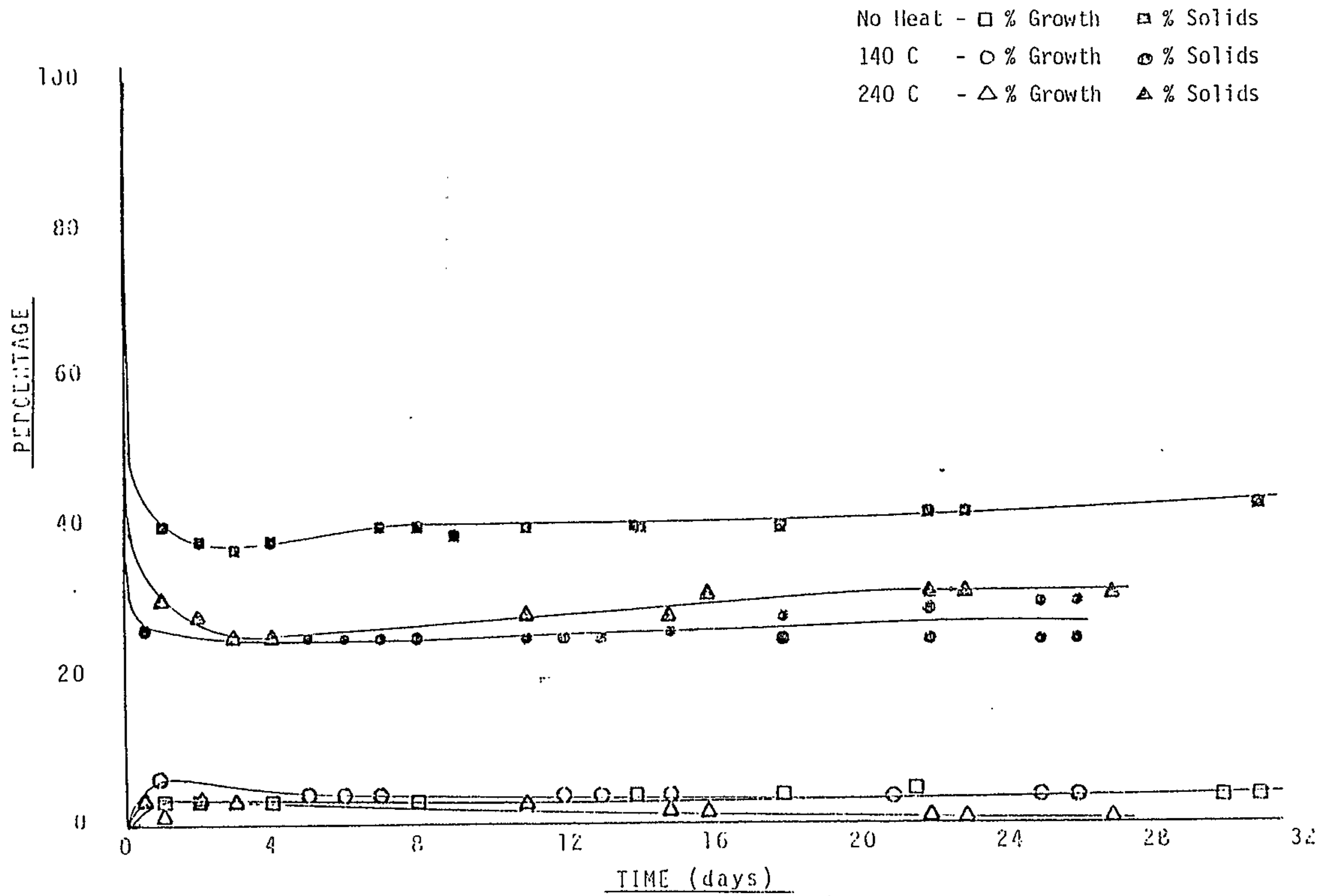


FIGURE 3. A Comparison of Volume Percent Solids and Volume Percent Growth versus Time of DSS Containing No Organic Complexants.

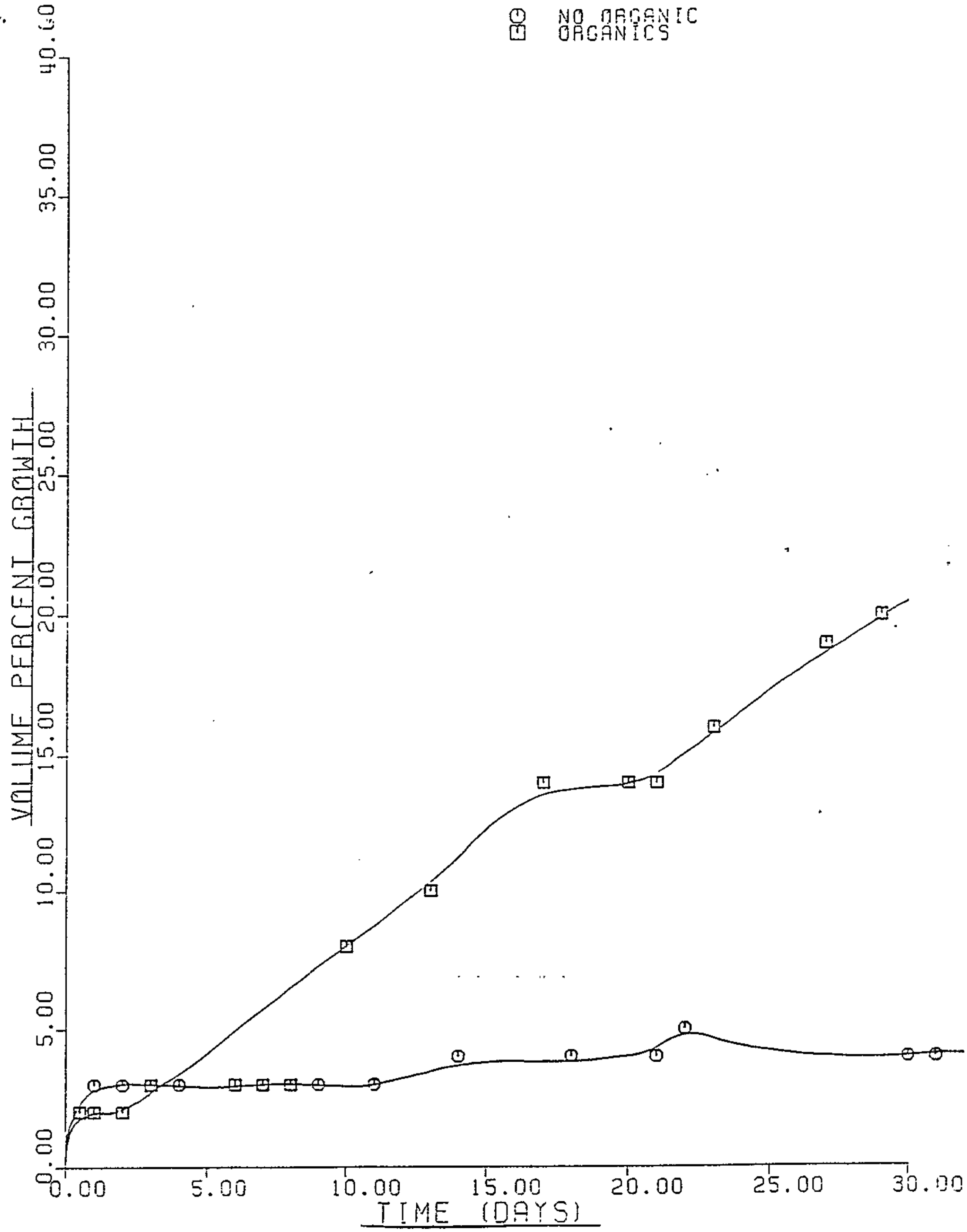


FIGURE 4. A COMPARISON OF VOLUME PERCENT GROWTH OF DSS WITH ORGANICS AND DSS WITHOUT ORGANICS, IN WHICH THE FEED SOLUTIONS WERE NOT THERMALLY PRETREATED.

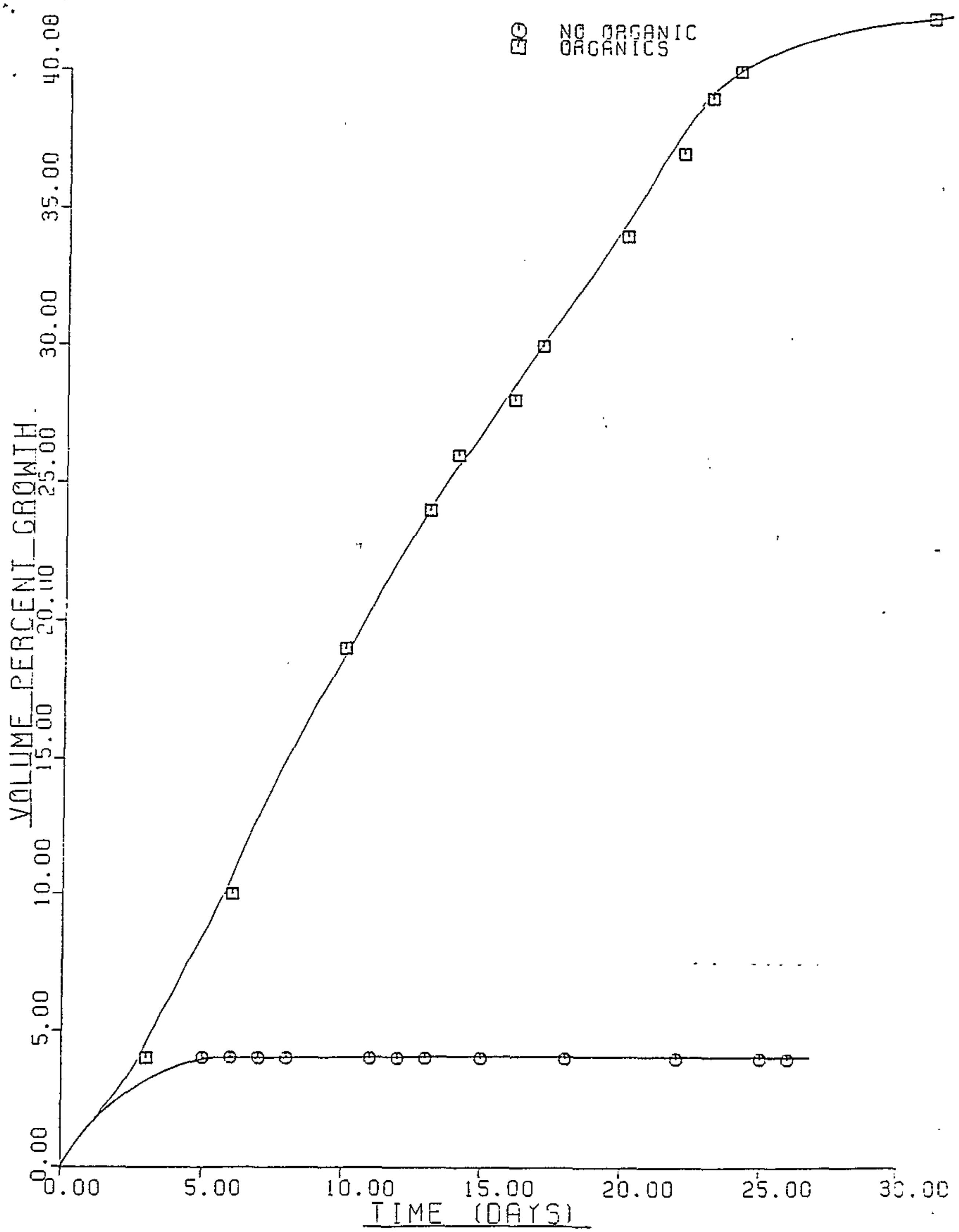


FIGURE 5. A Comparison of Volume Percent Growth of DSS with Organics and DSS without Organics, in which the feed solutions were heated to 140°C for 48 hours.

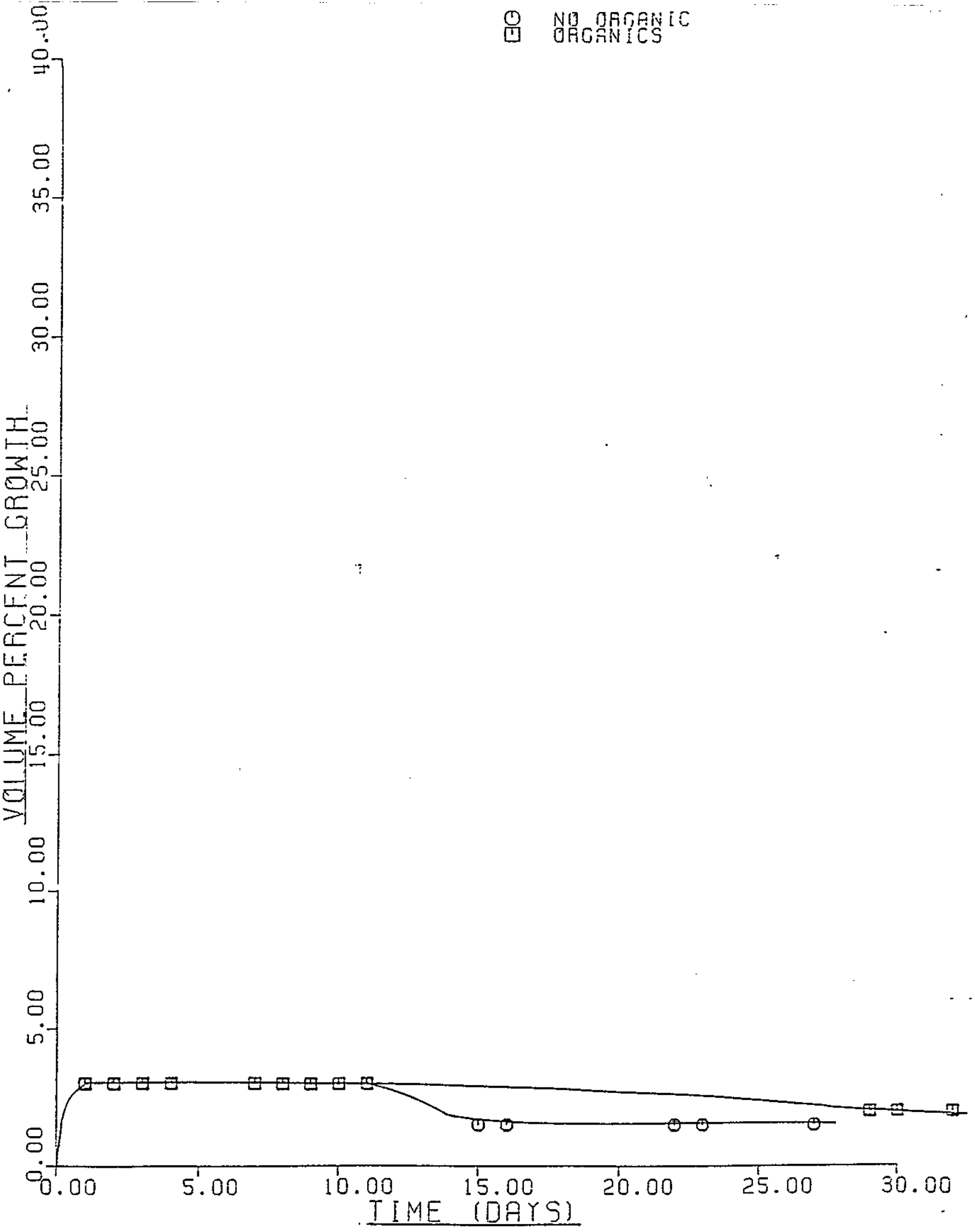


FIGURE 6. A COMPARISON OF VOLUME PERCENT GROWTH OF DSS WITH ORGANICS AND DSS WITHOUT ORGANICS, IN WHICH THE FEED SOLUTIONS WERE HEATED TO 240°C FOR 48 HOURS.

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